Efficient Procedure to Compute the Microcanonical Volume of Initial Conditions that Lead to Escape Trajectories from a Multidimensional Potential Well

Waalkens, Holger; Burbanks, Andrew; Wiggins, Stephen

Published in:
Physical Review Letters

Publication date:
2005

Efficient Procedure to Compute the Microcanonical Volume of Initial Conditions that Lead to Escape Trajectories from a Multidimensional Potential Well

Holger Waalkens, Andrew Burbanks, and Stephen Wiggins

School of Mathematics, University Walk, University of Bristol, Bristol BS8 1TW, United Kingdom

(Received 21 December 2004; revised manuscript received 10 March 2005; published 18 August 2005)

A procedure is presented for computing the phase space volume of initial conditions for trajectories that escape or "react" from a multidimensional potential well. The procedure combines a phase space transition state theory, which allows one to construct dividing surfaces that are free of local recrossing and that minimize the directional flux, and a classical spectral theorem. The procedure gives the volume of reactive initial conditions in terms of a sum over each entrance channel of the well of the product of the phase space flux across the dividing surface associated with the channel and the mean residence time in the well of trajectories which enter through the channel. This approach is illustrated for HCN isomerization in three dimensions, for which the method is several orders of magnitude more efficient than standard Monte Carlo sampling.

DOI: 10.1103/PhysRevLett.95.084301 PACS numbers: 45.20.Jj, 05.45.−a, 34.10.+x, 82.20.Db

Introduction.—In this Letter, we are concerned with the ubiquitous problem of escape from a potential well where exit is possible through channels that are associated with saddle points. We present a procedure that enables one to compute the phase space volumes of initial conditions in the well that leads to trajectories which escape from the potential well through any of these channels. The procedure relies on a recently developed *phase space* approach to transition state theory based on general ideas from dynamical systems theory [1,2]. Transition state theory was invented in the 1930s independently by Eyring and Wigner to compute chemical reaction rates [3]. In recent years, transition state theory has been proven to be a very powerful approach in a large, and diverse, number of applications which include ionization problems in atomic physics [4], rearrangements of clusters [5], escape and capture problems in celestial mechanics [6] and cosmology [7], and transport problems in solid state and semiconductor physics [8,9]. The fundamental element of transition state theory is a dividing surface which locally divides the energy surface into two disjoint components and which is free of local "recrossing." These properties are crucial for rate computations. The problem of how to define and construct a dividing surface with these properties was solved for 2 degrees of freedom in the 1970s by Pechukas, Pollak, and others [10], who constructed the dividing surface from a periodic orbit, the so-called periodic orbit dividing surface. The generalization to systems with more than 2 degrees of freedom has posed severe problems. Periodic orbits lack sufficient dimensionality for the construction of dividing surfaces for systems with 3 or more degrees of freedom. A fundamentally new object, a normally hyperbolic invariant manifold (NHIM), has to take the place of the periodic orbit. The NHIM is the main building block of the phase space transition state theory mentioned above.

In this Letter, we show that a combination of phase space transition state theory and a so-called classical "spectral theorem" proven by Pollak [11] gives an efficient procedure to compute the microcanonical volume of reactive initial conditions in a multidimensional potential well. We illustrate the procedure for HCN isomerization, which is a benchmark problem for reaction rate computations and of much current interest as a benchmark problem for understanding issues related to the control of chemical reactions [12]. We first recapitulate the building blocks of the phase space transition state theory.

Phase space transition state theory.—We start with an equilibrium point for Hamilton's equations which is of the saddle-center-...-center type (which we refer to as "saddle" for short, in what follows). A detailed theory for phase space transport near saddles has been developed in recent years [1]. For energies slightly above that of a saddle, on each $(2n-1)$-dimensional energy surface, with n being the number of degrees of freedom, there exists an invariant $(2n-3)$-dimensional sphere S^{2n-3} of saddle stability type with two important properties.

First, it is the "equator" of a particular $(2n-2)$-dimensional sphere, which we take as the dividing surface (DS). The equator separates the dividing surface into two hemispheres with the structure of open $(2n-2)$-dimensional balls. Except for the equator (which is an invariant manifold), the dividing surface is locally a "surface of no return": trajectories which have crossed the dividing surface must leave a certain neighborhood of the dividing surface before they can possibly cross it again. The dividing surface satisfies the *bottleneck property*. This means that the energy surface has *locally* the structure of $S^{2n-2} \times I$ [i.e., $(2n-2)$-sphere $\times$ interval] and the dividing surface divides the energy surface into two disjoint components. Moreover, the *only* way a trajectory can pass from one component of the energy surface to the other in the "forward" direction is through one hemisphere, and the only way to pass in the "backward" direction is through the other hemisphere. The hemispheres, which we denote by $\mathrm{DS}_{\mathrm{exit}}$ and $\mathrm{DS}_{\mathrm{enter}}$, respectively, are thus gateways to the exit and entrance channels for the energy

surface components. The flux through the forward and backward hemispheres is of equal magnitude and opposite sign so that the total flux through the dividing surface is zero. The *directional* flux is minimal for the dividing surfaces that we construct [13].

Second, the $(2n-3)$ sphere is a NHIM [1]. Normal hyperbolicity means that the expansion and contraction rates of the dynamics on the $(2n-3)$ sphere are dominated by those transverse to it. The NHIM therefore has stable and unstable manifolds, which in this case are $(2n-2)$ dimensional, having the structure of *spherical cylinders*, $S^{2n-3}\times\mathbb{R}$. Hence, they are of one dimension less than the energy surface and act as "separatrices"; they "enclose" volumes of the energy surface. Their key dynamical significance is that the only way that trajectories can pass through the dividing surface is if they are inside a particular region of the energy surface enclosed by the spherical cylinders. These phase space structures can be computed via an algorithmic procedure based on Poincaré-Birkhoff normalization that is described in [2].

Classical spectral theorem.—We consider a single potential well in which entrance or exit is possible only through a number of dividing surfaces, DS_i, and compute the *energy surface volume* of reactive initial conditions. The phase space transport theory described above is crucial for this computation as it allows us to define entrance and exit channels uniquely in terms of dividing surfaces, having the property of "no recrossing of trajectories" and minimal directional flux.

As a consequence of Liouville's theorem on the conservation of phase space volume [14], the reactive initial conditions in the well lie (up to a set of measure zero) on trajectories which in the future escape from the well *and* in the past entered the well. Hence for each point on a particular dividing surface hemisphere $\mathrm{DS}_{i;\mathrm{enter}}$, there exists a time t (which depends on the point) for the trajectory starting at this point to escape through the same, or another, dividing surface. We define the *mean passage time associated with* $\mathrm{DS}_{i;\mathrm{enter}}$ as

$$\langle t\rangle_{i;\mathrm{enter}} = \left(\int_{\mathrm{DS}_{i;\mathrm{enter}}} t\Omega\right)\Big/\left(\int_{\mathrm{DS}_{i;\mathrm{enter}}} \Omega\right). \tag{1}$$

Here the measure is given by $\Omega=\omega^{n-1}/(n-1)!$, with ω being the symplectic two-form $\Sigma_{k=1}^{n} dp_k\wedge dq_k$. It then follows from arguments analogous to those that lead to the so-called classical spectral theorem proven by Pollak [11] in the context of bimolecular collisions that the energy surface volume of reactive initial conditions in a well is given by

$$N_{\mathrm{react}} = \sum_i \langle t\rangle_{i;\mathrm{enter}}\phi_{i;\mathrm{enter}}, \tag{2}$$

where the summation runs over each dividing surface hemisphere $\mathrm{DS}_{i;\mathrm{enter}}$ controlling access to the well, and each channel contributes to the total volume by the product of the associated mean passage time and the flux,

$$\phi_{i;\mathrm{enter}} = \int_{\mathrm{DS}_{i;\mathrm{enter}}} \Omega. \tag{3}$$

The mean passage time can be computed from a Monte Carlo sampling of the DS hemisphere. Performing such a sampling, uniformly with respect to the measure Ω, is straightforward in the normal form coordinates. The flux through a dividing surface hemisphere is also computed easily from the normal form [13].

Application to HCN isomerization.—In order to illustrate how formula (2) can be used, we apply it to the HCN isomerization problem [12]. Restricting to vanishing angular momentum, the system has 3 DOF, the Jacobi coordinates: r (distance between C and N), R (distance between H and the center of mass of C and N), and γ (angle between H and C as seen from the center of mass of C and N). The corresponding Hamiltonian is

$$H = \frac{1}{2\mu}p_r^2 + \frac{1}{2m}p_R^2 + \frac{1}{2}\left(\frac{1}{\mu r^2}+\frac{1}{mR^2}\right)p_\gamma^2 + V(r,R,\gamma), \tag{4}$$

where $\mu = m_{\mathrm{C}}m_{\mathrm{N}}/(m_{\mathrm{C}}+m_{\mathrm{N}})$ is the reduced mass of the CN diatom, $m = m_{\mathrm{H}}(m_{\mathrm{C}}+m_{\mathrm{N}})/(m_{\mathrm{H}}+m_{\mathrm{C}}+m_{\mathrm{N}})$ is the reduced mass of the full system, and the potential V is taken from Murrell and co-workers [15]. There are two saddle points which are relevant for the isomerization. They are related by reflection symmetry and have $\gamma = \pm\gamma^* \approx \pm 67°$; see Fig. 1. We fix the energy at 0.2 eV above the saddle energy.

Figures 2(a) and 2(b) show a magnification of the neighborhood of the saddle in configuration space together with the configuration space projections of the $3d$ (phase space) NHIM and its $4d$ (phase space) stable and unstable manifolds calculated from the normal form. Figure 2(c) shows the $4d$ dividing surface. It completely fills the "bottle-

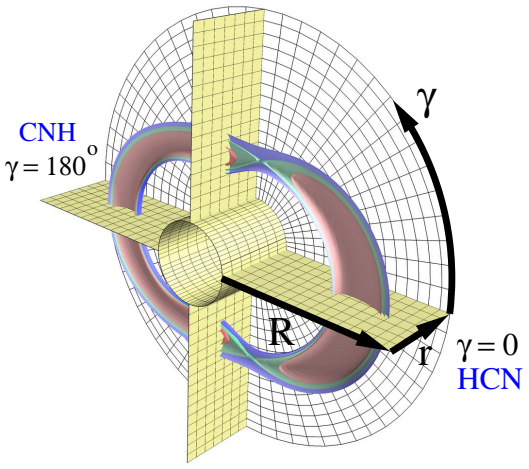

FIG. 1 (color online). Isopotential surfaces of the HCN potential energy surface of [15] in polar representation of the Jacobi coordinates r, R, and γ.

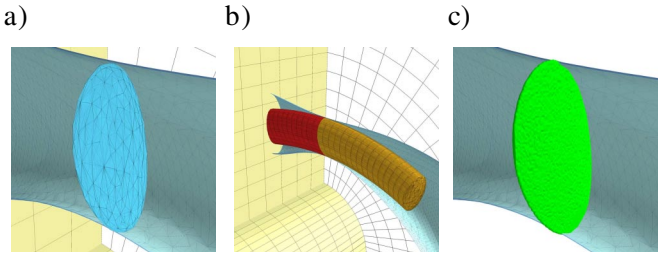

FIG. 2 (color online). Magnification of the neighborhood of the saddle at $\gamma = \gamma^*$ in Fig. 1 and the configuration space projection of cell complexes (meshes) constructed for visualization purposes on (a) the NHIM, (b) its stable and unstable manifolds, and (c) the dividing surface.

neck'' in the isopotential surface in configuration space and, more importantly, in the $5d$ energy surface.

The dividing surfaces near γ^* and $-\gamma^*$ divide the energy surface into two components: the component associated with the HCN well and the component associated with the CNH well. The only way a trajectory can pass from the HCN component to the CNH component or vice versa is through one of the dividing surfaces.

We use Eq. (2) to compute the energy surface volume of initial conditions in the HCN component which leads to trajectories that react to the CNH well. By symmetry,

$$N_{\mathrm{HCN;react}} = 2\langle t\rangle\phi, \tag{5}$$

where $\langle t\rangle$ is the mean passage time that trajectories starting on the hemisphere of the dividing surface near $\gamma = \gamma^*$, which correspond to reaction from CNH to HCN, spend in the HCN component before escaping, and ϕ is the flux through this dividing surface hemisphere. The mean passage time, computed from a Monte Carlo integration, is found to be $\langle t\rangle = 0.174$ ps. The rapid convergence to this value, as the number of sample points is increased, is illustrated in Fig. 3(a). We compute the flux ϕ using the normal form following the procedure in [13] and find $\phi = 0.0085\ h^2$, where h denotes Planck's constant. Hence, using (5), we have

$$N_{\mathrm{HCN;react}} = 0.0717\ h^2/\mathrm{eV}. \tag{6}$$

In order to illustrate the validity of this result, we perform a completely independent brute-force Monte Carlo computation of $N_{\mathrm{HCN;react}}$. To this end we uniformly sample initial conditions with respect to the measure $\delta(E - H)drdRd\gamma dp_r dp_R dp_\gamma$ in the HCN component and integrate them until they escape to the CNH component. Figure 3(b) shows the resulting survival probability $P_s(t)$, i.e., the normalized histogram of trajectories that stay in the HCN component up to time t. The survival probability $P_s(t)$ saturates for $t \to \infty$ at a value $P_s(\infty)$, which can be interpreted as the fraction of initial conditions in the HCN component that is nonreactive. Likewise, $1 - P_s(\infty)$ can be interpreted as the fraction of reactive initial conditions in the HCN component, i.e., $1 - P_s(\infty) = N_{\mathrm{HCN;react}}/N_{\mathrm{HCN}}$,

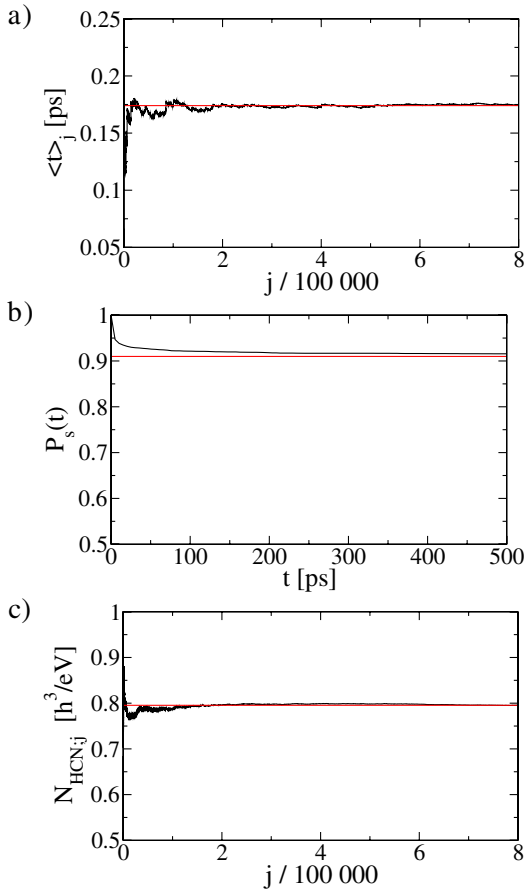

FIG. 3 (color online). (a) Monte Carlo computation of mean passage time $\langle t\rangle_j$ as a function of the number of sample points j. (b) Survival probability of trajectories with initial conditions in the HCN component (the units along the time axis are picoseconds). (c) Convergence of a Monte Carlo computation of energy surface volume $N_{\mathrm{HCN};j}$ as a function of the number of sample points j.

where N_{HCN} is the total energy surface volume of the HCN component. Now N_{HCN} can be obtained as a by-product of the Monte Carlo sampling which gave the survival probability, *without integrating trajectories*, and it is found to be $N_{\mathrm{HCN}} = 0.795\ h^3/\mathrm{eV}$. Convergence to this value as a function of the number of sample points is shown in Fig. 3(c). The value for $P_s(\infty)$, computed by our method, is shown as the horizontal line in Fig. 3(b). We note that the agreement with the saturation value of the survival probability is excellent.

A comparison of the computational effort required for the brute-force Monte Carlo calculation of the reactive volume with that required to implement (5) can be made as follows. Suppose one needs M sample points on the dividing surface $\mathrm{DS}_{\mathrm{enter}}$ to reach a predefined accuracy. On average, for HCN isomerization, one has to integrate the corresponding trajectories for 0.174 ps, which we have computed as the average passage time for trajectories entering the HCN well. To reach the same accuracy using the brute-force Monte Carlo method, one would have to

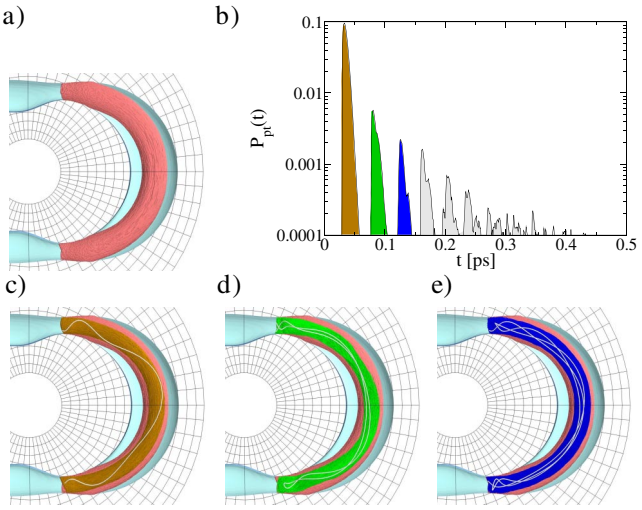

FIG. 4 (color online). Configuration space projection of the volume of reactive initial conditions [(a); pink (gray)] in the HCN energy surface component, and subvolumes that are filled out by trajectories that enter the HCN component, perform one [(c); brown (shaded subvolume)], two [(d); green (shaded subvolume)], or three [(e); blue (shaded subvolume)] oscillation(s) in the HCN well before escaping. Panels (c)–(e) also show a representative trajectory of the relevant type. (b) Distribution of passage times $P_{pt}(t)$ for initial conditions on the DS hemisphere controlling access to the HCN well.

sample $10 \times M$ points (because, roughly, only 9% of initial conditions in the HCN well react), which, on average, one would have to integrate for a much longer time (of the order of some cutoff time, for which we have found 500 ps sufficient to ensure accuracy). This gives roughly a ratio 1:30 000 for the efficiency (for this cutoff time). The fact that only 9% of initial conditions in the HCN well correspond to reactive trajectories has serious implications for any type of sampling strategy. Unless some insight is used, a method that ignores the dynamics, or makes recourse to assumptions of ergodicity, is bound to be inefficient.

Our recent advances in computational methods allow us to compute the ''reactive volumes'' (i.e., the relevant volumes enclosed by the appropriate stable and unstable manifold branches of the NHIM) and, for example, to visualize their projections into the configuration space; see Fig. 4(a). While only 9% of trajectories in this well undergo reaction, the projection of their $5d$ phase space volume into configuration space gives the appearance that far more trajectories react. This is an instance of how the configuration space point of view can give a misleading picture of the dynamics. Figures 4(c)–4(e) show subvolumes of the reactive volume that are filled out by trajectories of a specific type. Namely, the total reactive volume is comprised of subvolumes corresponding to trajectories that enter the well and make a fixed number of oscillations in the well. This behavior is elucidated by computing the distribution of passage times, shown in Fig. 4(b), for trajectories starting on one of the dividing surface hemispheres controlling access to the HCN well. Here we see that passage times for trajectories entering the well from this dividing surface occur in separated, discrete time intervals. The first three peaks in this figure correspond to the reactive subvolumes in Figs. 4(c)–4(e), respectively.

Conclusions.—We have presented a method which enables one to compute the microcanonical volumes of reactive initial conditions from the *exact* dynamics which is computationally much more efficient than brute-force Monte Carlo sampling approaches. As indicated in the example shown, it opens the way to study fundamental questions in the context of transition state theory, such as non–Rice-Ramsberger-Kassel-Marcus behavior and memory effects—no ergodicity assumptions or modifications of the dynamics are required.

This work was supported by the Office of Naval Research, the EPSRC, and the Royal Society.

[1] S. Wiggins, Physica (Amsterdam) **44D**, 471 (1990); S. Wiggins, *Chaotic Transport in Dynamical Systems* (Springer, Berlin, 1992); S. Wiggins, *Normally Hyperbolic Invariant Manifolds in Dynamical Systems* (Springer, Berlin, 1994); S. Wiggins, L. Wiesenfeld, C. Jaffé, and T. Uzer, Phys. Rev. Lett. **86**, 5478 (2001); H. Waalkens, A. Burbanks, and S. Wiggins, J. Chem. Phys. **121**, 6207 (2004).
[2] T. Uzer, C. Jaffé, J. Palacián, P. Yanguas, and S. Wiggins, Nonlinearity **15**, 957 (2002).
[3] H. Eyring, J. Chem. Phys. **3**, 107 (1935); E. Wigner, Trans. Faraday Soc. **34**, 29 (1938).
[4] C. Jaffé, D. Farrelly, and T. Uzer, Phys. Rev. Lett. **84**, 610 (2000).
[5] T. Komatsuzaki and R. S. Berry, J. Chem. Phys. **110**, 9160 (1999).
[6] C. Jaffé, S. D. Ross, M. W. Lo, J. Marsden, D. Farrelly, and T. Uzer, Phys. Rev. Lett. **89**, 011101 (2002).
[7] H. P. de Olivieira, A. M. Ozorio de Almeida, I. Damião Soares, and E. V. Tonini, Phys. Rev. D **65**, 083511 (2002).
[8] G. Jacucci, M. Toller, G. DeLorenzi, and C. P. Flynn, Phys. Rev. Lett. **52**, 295 (1984).
[9] B. Eckhardt, J. Phys. A **28**, 3469 (1995).
[10] P. Pechukas and F. J. McLafferty, J. Chem. Phys. **58**, 1622 (1973); P. Pechukas and E. Pollak, J. Chem. Phys. **69**, 1218 (1978); P. Pechukas, Annu. Rev. Phys. Chem. **32**, 159 (1981).
[11] E. Pollak, J. Chem. Phys. **74**, 6763 (1981).
[12] H. Tang, S. Jang, M. Zhao, and S. A. Rice, J. Chem. Phys. **101**, 8737 (1994); J. Gong, A. Ma, and S. A. Rice, J. Chem. Phys. **122**, 144311 (2005).
[13] H. Waalkens and S. Wiggins, J. Phys. A **37**, L435 (2004).
[14] V. I. Arnol'd, *Mathematical Methods of Classical Mechanics* (Springer, Berlin, 1978).
[15] J. N. Murrell, S. Carter, and L. O. Halonen, J. Mol. Spectrosc. **93**, 307 (1982).